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Vanadium Recovery from Oil Fly Ash by Carbon Removal and Roast-Leach Process

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This research mainly focuses on the recovery of vanadium from oil fly ash by carbon removal and the roast-leach process. The oil fly ash contained about 85% unburned carbon and 2.2% vanadium by weight. A vanadium-enriched product was obtained after carbon removal, and the vanadium content of this product was 19% by weight. Next, the vanadium-enriched product was roasted with sodium carbonate to convert vanadium oxides to water-soluble sodium metavanadate. The roasted sample was leached with water at 60°C, and the extraction percentage of vanadium was about 92% by weight. Several analytical techniques, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), x-ray fluorescence (XRF), and thermogravimetric and differential thermal analysis (TG–DTA), were utilized for sample analyses. Thermodynamic modeling was also conducted with HSC chemistry software to explain the experimental results.

INTRODUCTION

According to the US Energy Information Administration, major energy sources of the electricity generation, such as coal, natural gas, nuclear, hydropower, and other renewables, were generating 99% of the total US electricity in 2015. Only 1% of the total electricity was generated from petroleum; however, petroleum-based power plants consumed about 29 million barrels of petroleum liquids and 4 million tons of petroleum coke in 2015.[1] From this point of view, huge amounts of waste are being generated by power plants, one of which is oil fly ash. Fly ash is a fine dust generated during the combustion of fossil fuel that is mostly captured by electrostatic precipitator or other dust collection systems. The main characteristics of oil fly ash are the high concentrations of unburned carbon and vanadium.[2,3] Therefore, researchers have been focused on its use as a secondary source for vanadium. For example, Vitolo et al. accomplished 83% vanadium recovery from a previously burned heavy oil fly ash using several stages, such as preliminary burning, acid leaching, and oxidative precipitation.[3] Navarro et al. also studied vanadium recovery from oil fly ash and could extract 61% of vanadium by sodium hydroxide leaching with aluminum as an impurity.[4] Abdel-latif utilized petroleum fly ash as a source of vanadium and nickel for ferrovanadium alloy production.[5] These studies mostly used acid or alkaline reagents to dissolve vanadium; however, reagent cost could affect the overall feasibility of the recycling process.

In this research, oil fly ash was provided from an oil-fired power plant in Texas, and the sample was analyzed with several analytical techniques. Vanadium recovery from oil fly ash was conducted by carbon burning and roast-leach processes. Water was selected as a reagent to extract vanadium from the sample. In addition to the experimental study, thermodynamic analyses of the carbon removal and salt roasting were also carried out with HSC chemistry.

EXPERIMENTAL

Initial Analyses of As-Received Oil Fly Ash

Initial analysis of the as-received oil fly ash was conducted with inductively coupled plasma atomic emission spectroscopy (ICP-AES) and x-ray fluorescence (XRF). For the ICP sample preparation, 0.1 g of as-received oil fly ash was mixed with 1 g lithium borate mixture, 60% lithium metaborate, and 40% lithium tetraborate by weight for a better dissolution of refractory metal oxides in a graphite crucible.[6] The sample was heated at 1000°C for 1 h in a

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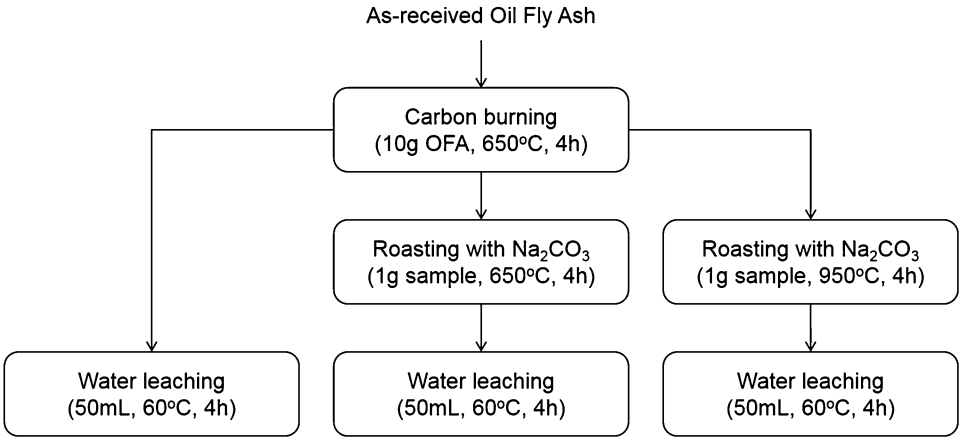

Fig. 1. Proposed flow sheet of vanadium extraction.

muffle furnace, and the melt was digested with 100 ml 25% nitric acid at 60°C. Lastly, the metal-containing solution was diluted with 2% nitric acid. For representative ICP results, five different samples were analyzed with the same method. XRF was also used for bulk chemical analysis of the oil fly ash. To this end, 2 g of the oil fly ash was pressed with boric acid powder to prepare pellets for the analysis. In addition to the chemical analysis, loss on ignition (LOI) measurement and thermogravimetric and differential thermal analysis (TG–DTA) were conducted for the sample characterization.

Vanadium Extraction by Carbon Burning and Roast-Leach Processes

Three different steps, such as carbon burning, salt roasting, and water leaching, were conducted to extract vanadium from the oil fly ash. First, a vanadium-enriched product could be obtained after carbon removal since the material contained a huge amount of unburned carbon. Ten grams of as-received fly ash was transferred to a porcelain crucible and heated in a muffle furnace at 650°C for 4 h to minimize sample loss due to the melting. After that, 1 g of the vanadium-enriched product was mixed with sodium carbonate (1.06 g, 2.12 g, and 3.18 g) and subsequently roasted in a muffle furnace at two different temperature conditions (650°C and 950°C) for 4 h to convert vanadium oxides to a yellow-colored sodium vanadate ($NaVO_3$), which is a water-soluble vanadium compound. Prior research has used acid or alkaline reagents for better vanadium extraction;[7–9] however, we selected water for the reagent. The salt-roasted product was mixed with 50 ml of water to minimize solubility effects, and vanadium in the product was selectively dissolved at 60°C for 4 h. Figure 1 shows a summary of the experimental conditions for vanadium extraction.

RESULTS AND DISCUSSION

Initial Characterization of As-Received Oil Fly Ash

Based on the ICP result as shown in Table I, the sample contained about 2.2% vanadium and 1.9% iron by weight. Additionally, XRF results indicated 3.9% vanadium oxide and 1.6% ferric oxide. Oil fly ash had about 4.5% metallic elements or 6.6% metal oxides because of a large amount of unburned carbon. Therefore, LOI of the oil fly ash was measured to check the total amount of volatile matter, such as moisture, sulfur, and carbon, based on the ASTM D7348.

As shown in Table II, the percentage of LOI at 650°C was about 87%, and it indicated the total amount of volatile matter in the oil fly ash was about 87%. Additionally, TG–DTA was conducted to check the weight changes with different sample temperatures. As shown in Fig. 2, moisture in the sample was evaporated, and carbon burning was started at a temperature above 450°C. The total weight reduction from the oil fly ash was about 89%, which was identical to the LOI result. The amount of weight reduction due to the carbon removal was about 85% by weight. For this reason, the carbon removal process was an essential step to obtain a vanadium-enriched product.

Carbon Removal to Obtain Vanadium-Enriched Product

Oil fly ash contained about 89% volatile matter, mostly unburned carbon. Once the carbon was removed from the sample, a vanadium-enriched product could be obtained for the further vanadium recovery process. Therefore, 10 g of the oil fly ash was heated in a muffle furnace at 650°C for 4 h. After the carbon removal process, the vanadium concentration in the sample was increased from

Table I. Chemical compositions of as-received oil fly ash

ICP analysis		XRF analysis	
Element	**Wt.%**	**Compound**	**Wt.%**
Al	0	Al_2O_3	0.1
Ca	0	CaO	0.1
Fe	1.9	Fe_2O_3	1.6
Ni	0.4	NiO	0.7
Si	0	SiO_2	0.2
V	2.2	V_2O_5	3.9
Ti	0	TiO_2	0
C	Balance	C	Balance

Table II. Loss on ignition of as-received fly ash at 650°C

Time (h)	Initial mass (g)	Final mass (g)	LOI (%)
1	10.046	3.089	69.25
2	10.149	1.354	86.66
3	10.012	1.634	83.68
4	10.392	1.322	87.28

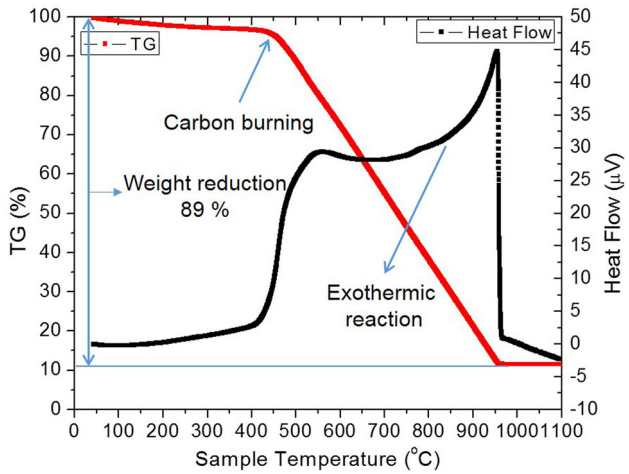

Fig. 2. TG–DTA analysis of as-received oil fly ash.

2.2% to 19% by weight, as shown in Table III. Additionally, iron and nickel concentrations were increased to 12.7% and 4.1%, respectively. From the result, a vanadium-enriched product was obtained after the carbon removal process at 650°C for 4 h.

Thermodynamic Study of Carbon Removal and Salt-Roasting Process

Thermodynamic study of carbon removal and salt roasting was conducted with HSC chemistry to check the stable phase of vanadium oxides in the vanadium-enriched product after carbon removal. Phase stability diagrams of V-C-O at 650°C are plotted, as shown in Fig. 3. Based on Fig. 3a, the formation of vanadium pentoxide was thermodynamically favorable when the log $pO_2(g)$ was greater than − 4 and the log pCO(g) less than 3. When $CO_2(g)$ atmosphere was considered during the carbon removal process, the formation of vanadium pentoxide was favorable at a log $pCO_2(g)$ below 18, as shown in Fig. 3b.

The purpose of the salt-roasting process is to convert vanadium oxides to the water-soluble sodium metavanadate ($NaVO_3$). Thermodynamic study of the salt-roasting process was also conducted with HSC chemistry. Based on Fig. 3, vanadium pentoxide was the stable phase after the carbon burning process since the process was conducted near the marked area with airflow. Therefore, a reaction equation was proposed during the salt-roasting process, and the changes in Gibbs free energy at different temperature conditions were as follows:

$$V_2O_5 + Na_2CO_3 = 2NaVO_3 + CO_2(g) \qquad (1)$$

$$\Delta G \text{ at } 600^\circ C = -36.5 \text{ kcal/mol}$$

$$\Delta G \text{ at } 800^\circ C = -44.4 \text{ kcal/mol}$$

$$\Delta G \text{ at } 1000^\circ C = -50.2 \text{ kcal/mol}$$

Based on the thermodynamic data, the formation of sodium metavanadate was favorable at temperatures between 600°C and 1000°C since the change in Gibbs free energy of the reaction showed negative values.

Table III. Effect of carbon removal process from as-received fly ash (10 g of sample, 650°C, 4 h)

ICP-AES	As-received oil fly ash	Vanadium-enriched product
Element	Composition, wt.%	Composition, wt.%
Al	0	1.2
Fe	1.9	12.7
Ni	0.4	4.1
V	2.2	19.0

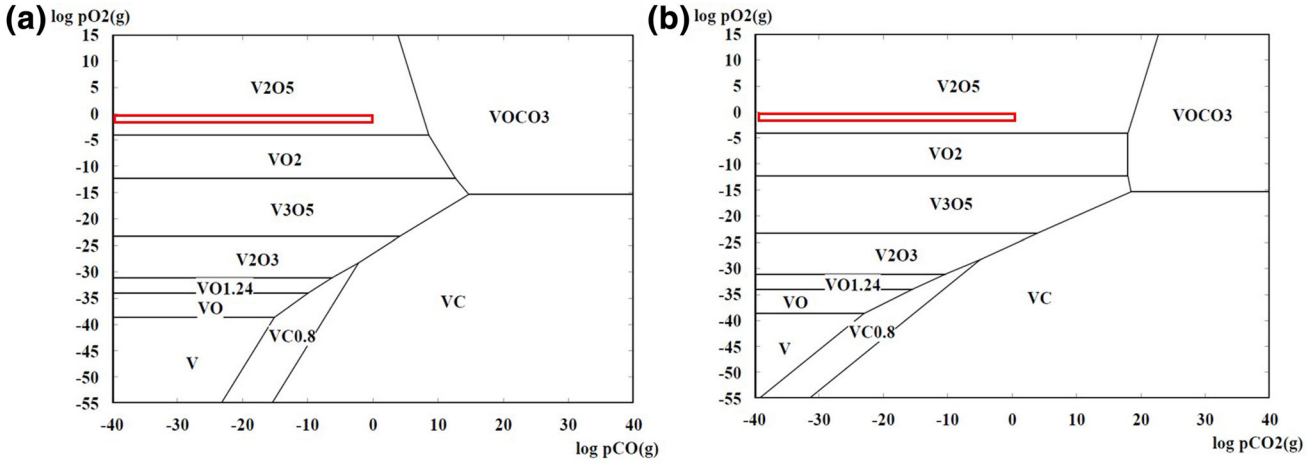

Fig. 3. Phase stability diagram of the V-C-O condition at 650°C: (a) log pCO versus log pO_2; (b) log pCO_2 versus log pO_2.

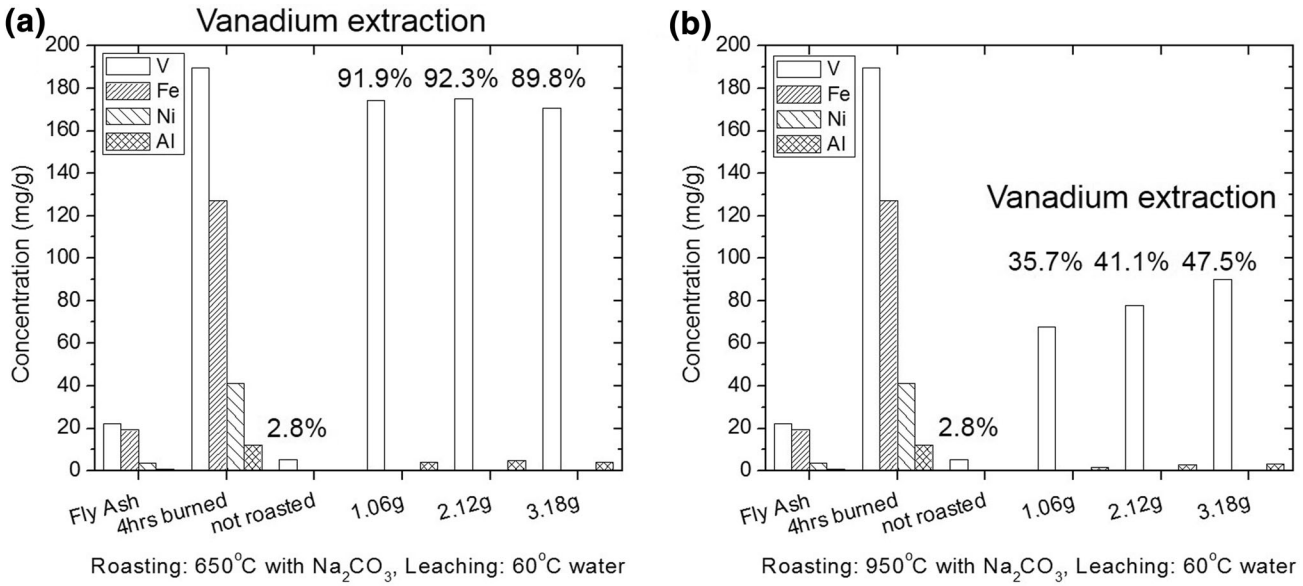

Fig. 4. The percentage of vanadium extraction after the roast-leach process: (a) roasted at 650°C; (b) roasted at 950°C.

Effect of Salt-Roasting Temperature on Vanadium Recovery

Three different routes of vanadium extraction, such as no roasting, roasting at 650°C, and roasting at 950°C, were compared to check the effect of salt roasting and its temperature on vanadium extraction. Based on Eq. 1, vanadium pentoxide required the same mole of sodium carbonate for the reaction stoichiometry. Since the vanadium concentration in the vanadium-enriched sample was about 19% by weight, the sample had about 0.0037 mol of vanadium, and this value was equivalent to 0.0019 mol of vanadium pentoxides. Thus, different amounts of sodium carbonate (1.06 g, 2.12 g, and 3.18 g) were mixed with the vanadium-enriched product for the roasting.

Figure 4 shows the percentage of vanadium extraction at different conditions. During the salt roasting at 950°C, vanadium oxide melts and sticks to the crucible surface since the melting point of vanadium pentoxide is 690°C. This phenomenon affected the vanadium extraction through water leaching since the reaction between sodium metavanadate and water occurred only at the surface. When the salt roasting was conducted at 650°C, there was no sample melting and sticking, and it guaranteed a better vanadium extraction, as seen in Fig. 4a. The percentage of vanadium extraction was about 92% after salt roasting at 650°C; however, only 3% of vanadium was extracted without the salt-roasting process. This result supported the formation of water-soluble sodium

metavanadate after the salt-roasting process and was an essential step for efficient vanadium recovery.

On the other hand, the percentage of vanadium extraction was decreased from 92% to 36% with 1.06 g of sodium carbonate addition at 950°C. At this roasting temperature, vanadium extraction was increased with the amount of sodium carbonate from 36% to 48%; however, the roasted sample stuck to the crucible surface and was not extractable. After carbon burning, iron and nickel contents were increased; however, water could selectively dissolve vanadium from the roasted sample. Therefore, a three-step process including carbon burning, salt roasting, and water leaching could be an effective method for vanadium recovery.

CONCLUSION

This research focused on the characterization of oil fly ash and the vanadium recovery. As-received fly ash contained about 85 wt.% of carbon and 2.2 wt.% of vanadium. Vanadium content in the sample was concentrated from 2.2 wt.% to 19 wt.% after the carbon removal. Ninety-two percent of vanadium was recovered selectively by leaching in water after salt roasting at 650°C with sodium carbonate. Since water leaching did not dissolve iron and nickel from the sample, the leach solution predominantly comprised the vanadium compound.

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